# VII.8 LSGM-Based Composite Cathodes for Anode-Supported, Intermediate-Temperature (600-800°C) Solid Oxide Fuel Cells

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## Objectives

- Develop Sr- and Mg-doped $LaGaO_3$ (LSGM)-based composite cathodes for anode-supported solid oxide fuel cells (SOFCs) capable of operating at 600-800°C.
- Develop and optimize a powder synthesis process that produces single-phase, nanosized powders of LSGM and Co- and Fe-doped LSGM for cathode use.
- Optimize composite cathode interlayer with regards to microstructure and composition for low-temperature SOFC operation.
- Perform electrochemical testing on single cells at temperatures between 500 and 800°C and estimate electrode overpotentials and ohmic losses.
- Construct and demonstrate the operation of an internally manifolded stack, comprised of cells with LSGM-based cathodes, capable of delivering 1 kW of power while operating on partially reformed natural gas at 800°C.

## Approach

- Identify mixed ionic-electronic conducting (MIEC) electrocatalytic materials compatible with LSGM for use in composite cathodes.
- Synthesize single-phase and nanosized powders of both electrocatalytic materials (MIEC) and LSGM by a glycine-nitrate combustion technique.
- Fabricate anode-supported SOFC with thin-film yttria-stabilized zirconia (YSZ) electrolytes for testing and evaluation of composite cathodes.
- Fabricate LSGM-based composite cathodes onto SOFC by screen printing. Optimize cathode with regards to thickness, particle size, composition, firing temperature, and firing time.
- Perform electrochemical testing of single SOFC at temperatures between 600 and 800°C.
- Characterize microstructure of the starting powders and the as-fabricated composite cathodes by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

## Accomplishments

- Successfully synthesized single-phase, nanosized powders of LSGM ($La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$) and various electrocatalytic materials including $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.6}Sr_{0.4}CoO_3$, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$, $La_2NiO_4$, and $La_{1.7}Sr_{0.3}NiO_4$.
- Fabricated and tested SOFCs with active areas of 2 $cm^2$ and 30 $cm^2$ with LSGM-based composite cathodes. Cell performance measured at temperatures between 600 and 800°C.

- Demonstrated that reduction in particle size and refinement of composite cathode interlayer microstructure can reduce the average area specific resistance (ASR) of the cell by as much as 25% for a given cathode composition.
- High performance in single cells with LSGM-based cathodes has been demonstrated. Power densities of 1.2 W/cm$^2$ at 0.7 V at 800°C, and 0.7 W/cm$^2$ at 0.7 V at 700°C, have been achieved.

## Future Directions

- Incorporate nanosized powders into composite cathode interlayer and optimize with respect to microstructure and processing conditions.
- Investigate the long-term stability of LSGM-based cathodes with respect to interdiffusion and secondary phase formation at operating temperatures.
- Further optimize the microstructure of LSGM-based cathodes containing Sr- and Fe-doped $LaCoO_3$ (LSCF), Sr-doped $LaCoO_3$ (LSC), and Sr-doped $LaFeO_3$ (LSF).
- Fabricate internally manifolded SOFC with LSGM-based cathodes and an active area of 100 cm$^2$. Evaluate the performance of the cells in short stacks.

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## Introduction

Previous work has shown that the largest polarization loss of an anode-supported SOFC with a thin-film electrolyte operating at 600 to 800°C is from the cathode. The polarization at the cathode can be substantially reduced by the use of composite cathodes that typically consist of a solid electrolyte, such as YSZ, and an electrocatalyst, such as $La_{1-x}Sr_xMn_{3-\delta}$ (LSM). The performance of the composite cathode depends on 1) oxide ion conductivity of the solid electrolyte (in the cathode), 2) the electronic and catalytic properties of the electrocatalyst, and 3) the microstructure of the composite cathode. Therefore, one approach to reducing the activation polarization of the composite cathode is to use a solid electrolyte phase that exhibits high oxide ion conductivity.

The perovskite oxide ion conductor $LaGaO_3$ doped with Sr and Mg (LSGM) exhibits higher oxide ion conductivity as compared to YSZ. Therefore, replacing the YSZ phase in the composite cathode with LSGM can substantially reduce the polarization losses at the cathode, especially at lower operating temperatures. In this work, composite cathodes comprised of LSGM and an electrocatalyst phase, such as LSC, LSF, or LSCF, have been developed and tested on anode-supported SOFCs. In addition, work is being done to develop and employ nanosized LSGM in the cathode interlayer to further reduce the polarization losses at the cathode.

## Approach

Anode-supported SOFCs were fabricated with composite cathodes comprised of LSGM and a number of electrocatalytic phases, including LSC, LSF, and LSCF. The cells consist of five distinct layers: a porous Ni/YSZ composite anode support (~1 mm), a porous Ni/YSZ anode interlayer (~15 μm), a dense thin-film YSZ electrolyte (~6-8 μm), a porous composite cathode interlayer (LSGM with either LSM or LSC) (~20 μm), and a porous current-collecting layer (LSM or LSC) (~50 um). In the case of the LSGM + LSC composite cathode, a barrier layer (~ 2 μm) of Gd-doped $CeO_2$ was deposited between the dense YSZ electrolyte and the composite cathode interlayer in order to prevent deleterious chemical reactions between the YSZ and LSC (Figure 1). Anode-supported cells with an active area of 2 cm$^2$ (button cells) and internally manifolded cells with an active area of 30 cm$^2$ have been fabricated and tested. Anodes were fabricated from NiO and YSZ mixtures by standard ceramic powder processes and tape casting. The dense electrolyte and barrier layers were fabricated by spraying powder suspensions followed by sintering. The composite cathodes were deposited by screen printing inks comprised of $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) and an electrocatalyst phase, such as $La_{0.85}Sr_{0.15}MnO_{3-\delta}$ (LSM) or $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ (LSC). A number of processing parameters have been varied in order to optimize the cathode microstructure and ultimately cell performance.

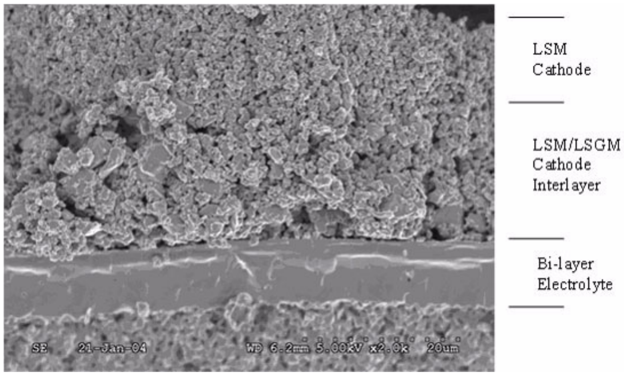


**Figure 1.** SEM Micrograph Showing a Cathode Interlayer Composed of LSGM and LSM

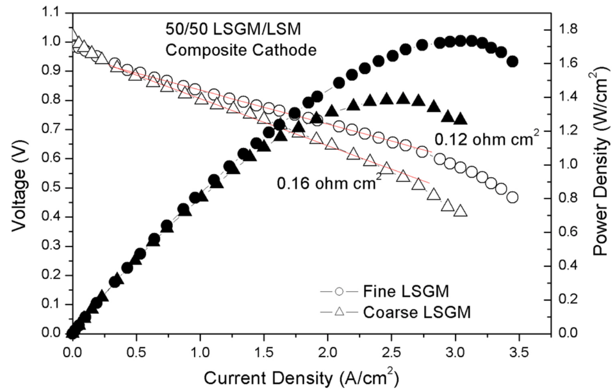


**Figure 2.** Performance of Two Cells with LSGM-LSM Cathodes Tested at 800°C, Showing the Effects of Particle Size on Cell Performance

For instance, a parametric study of cathode interlayer thickness, particle size, composition, firing temperature, and firing time is being conducted. Single cells were tested at temperatures between 600 and 800°C with flowing $H_2$ as the fuel and air as the oxidant. Currently, cells with an active area of 30 $cm^2$ and with LSGM-LSCF composite cathodes are being evaluated in SOFC stacks operating at 600 to 800°C.

The polarization losses at the cathode are largely a function of the microstructure, with a finer microstructure generally reducing the activation polarization. The development of a highly refined cathode microstructure is being conducted via the use of nanosized starting powders. The nanosized powders were synthesized by a combustion technique wherein the maximum measured temperatures were controlled and kept below 600°C to reduce effects of coarsening. An optimization of the processing parameters, including firing time and temperature, results in a finer microstructure with increased three-phase boundaries in the composite cathode layer.

## Results

Anode-supported cells with LSGM and the electrocatalyst phases LSM, LSC, LSF, and LSCF have been fabricated and tested. For each material combination, various parameters including composition of the cathode, particle size of the starting materials, firing times, and firing temperatures were systematically varied in order to optimize the performance of the composite cathode.

The performance of the composite cathode is largely dictated by microstructural parameters of the interlayer, including three-phase boundary (TPB) length, porosity, and contiguity of the electrocatalyst and solid electrolyte phases. The performance of the cathode is highly sensitive to the microstructure of the 15-20 µm composite interlayer. For instance, a reduction in particle size of the LSGM in the cathode interlayer can substantially increase the performance of the cell. Figure 2 shows the performance of two cells tested at 800°C with two different cathode layers, one having a cathode interlayer prepared with fine (submicron) LSGM powder and one prepared with coarse (2-3 µm) LSGM powder. In both cases, the anode substrates were prepared from the same batch and the cathode interlayer was the same composition, 50% LSGM and 50% LSM; thus, the only difference was particle size. The decrease in starting powder size produced a more refined cathode microstructure, resulting in a decrease in the ASR of the cell from 0.16 to 0.12 $\Omega cm^2$. This decrease in cell ASR translates into a power density of 1.4 W/ $cm^2$ at 0.7 V at 800°C. Further refinement of the cathode microstructure and improvements in cell performance are expected with the use of nanosized powders. Nanosized powders of LSGM and various electrocatalysts phases, including $La_{0.8}Sr_{0.2}MnO_3$, $La_{0.6}Sr_{0.4}CoO_3$, and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$, have been synthesized and characterized. The development and optimization of composite cathodes utilizing nanosized starting powders is currently being conducted.

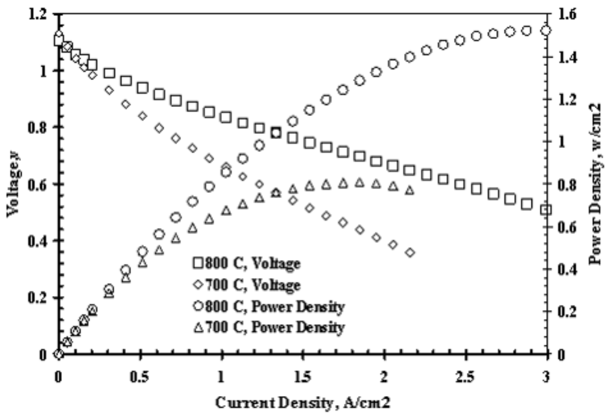


**Figure 3.** Performance of a Single Cell with a LSGM-LSCF Cathode Tested at 700 and 800°C

In addition to the microstructural effects, the intrinsic properties of the electrocatalytic phase play an important role in the activation polarization and ohmic losses of the cathode layers, especially at lower temperature. Although low cathode polarizations have been demonstrated with LSGM-LSM composite cathodes while operating at 800°C, the low electronic conductivity and semiconducting nature of LSM prohibits its use in the temperature range 600 to 700°C. In an effort to decrease the operating temperature of the SOFC, LSGM-based cathodes using the electrocatalytic phases LSC, LSF, and LSCF have been developed. The Fe- and Co-perovskite phases exhibit much higher electronic and ionic conductivity than LSM. However, these perovskite phases react with the YSZ electrolyte and, thus, a doped-ceria barrier layer is necessary to prevent the deleterious formation of any secondary phases. The performance of a cell with a LSGM-LSCF composite cathode layer tested at 700 and 800°C is shown in Figure 3. At 800°C, the power density of the cell is ~1.4 W/cm$^2$ at 0.7 V, and at 700°C, the power density is ~0.6 W/cm$^2$ at 0.7 V. The microstructure and starting powder particle size have not been fully optimized for this material system; thus, further increases in cell performance are expected with more refinement. After testing, the microstructure, composition, and crystal chemical properties of the composite cathode are characterized by SEM and XRD in order to detect formation of secondary phases and interdiffusion. To date, no secondary phases have been found, but some interdiffusion between LSGM and the other perovskite phases (electrocatalysts) can be detected after the cathode firing step. Further investigation of the effects of this interdiffusion on the performance and polarization losses of the composite cathode is underway.

## Conclusions

LSGM-based composite cathodes have been developed for anode-supported SOFCs with thin-film electrolytes, for operation in the temperature range 600 to 800°C. Cells with LSGM-LSM composite cathodes tested at 800°C have exhibited power densities as high as 1.4 W/cm$^2$ at 0.7 V.

The performance of the composite cathode interlayer is highly sensitive to microstructure and processing. For instance, a reduction in particle size of 50% in the cathode interlayer alone can decrease the ASR of the cell by as much as 25%. The incorporation of nanosized powders into the LSGM-based composite cathodes is currently underway. LSGM composite cathodes with the electrocatalysts LSC, LSF, and LSCF have been developed for lower temperature operation. Cells with LSGM-LSCF cathodes have delivered power densities of 0.6 W/cm$^2$ at 0.7 V at 700°C. In addition to cell-level testing, future work will include the testing of cells with LSGM-based cathodes in short stacks at temperatures between 600 and 800°C.

## FY 2004 Publications/Presentations

1. Poster presented at SECA Core Technology Program Review Meeting, September 30 - October 1, 2003. Albany, New York.